

The quality of alumina produced by the hydrochloric acid process and potential for improvement

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Abstract

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In the hydrochloric acid process, alumina is directed to calcination as aluminum chloride hexahydrate $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ (ACH). During the calcination process it loses approximately 80 % of its mass. This leads to physical and morphological characteristics of the product considerably different compared to those of smelter grade alumina (SGA), namely: fraction - 45 μm is above 60 mass %, which is six times greater than SGA; bulk density is lower than 0.35 g/cm^3 (about three times lower compared to SGA); flow time of approximately 22 minutes (about seven times greater than SGA), etc. So, alumina produced by the hydrochloric acid process has low bulk density and relatively high attrition index. The external surface of the particles is rough, which increases friction between particles and the angle of repose up to 32° and above, as well as the increased flow time from standard funnel test. All of the above prevents the use of alumina produced by the hydrochloric acid process in a modern high technology reduction process and requires research into process development aimed at modification of the physical, chemical and mechanical properties of alumina produced by acid method.

Keywords: Hydrochloric acid process; alumina calcination; aluminum chloride hexahydrate; smelter grade alumina flow time and bulk density; angle of repose.

1. Introduction

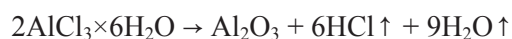
Actual commercial realization of SGA production by hydrochloric acid process from non-bauxite ore has revealed some challenges associated with chemical composition and physical-mechanical properties of the produced alumina.

Modern aluminum smelters are designed for processing of sandy grade SGA with strictly regulated characteristics. For example, particle size distribution should be in a narrow range from plus 45 to minus 150 μm ; particle shape should be close to isometric; particles should be resistant to attrition; special requirements to specific surface and absorption capacity to hydrogen fluoride, bulk density, angle of repose, flow time, etc., etc. All these properties of SGA are formed at earlier stages of the Bayer process, namely:

- In digestion for caustic- aluminate liquor generation with considerable Al_2O_3 supersaturation;
- In two stage precipitation with complex system of crystals and aggregates growth of specified form and size followed by classification of the produced aluminum hydroxide in several stages;
- In calcination in modern stationary calciners.

For alumina produced by the hydrochloric process, properties are formed at different process stages. After leaching of Al-silicates by HCl, alumina is transformed into liquor in form of $\text{AlCl}_3 \times \text{aq}$, next the product is precipitated (by crystallization) in form of aluminum chloride hexahydrate $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ (further ACH). The process modes during ACH crystallization affect the shape and size of crystals.

During thermal decomposition of ACH in the following reaction:



it loses 80 % of mass which obviously impacts the properties of the produced Al_2O_3 . This paper is dedicated to the study of the properties of aluminum oxide depending on process conditions.

2. Temperature and ACH thermal decomposition impact on phase analysis of produced alumina

With a calcination temperature of about 600 °C, near 20 % of the initial chloride from ACH remains in the calcination product in the form of aluminum oxychloride with general formula $\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}$. The other 80 % is removed in the form of HCl gas and water vapor while in the solid phase, forming the mix of polymorph aluminium oxide varieties with admixture of oxychloride of variable composition. With the increase of calcination temperature the volume of chlorine reduces.

Thermal decomposition of $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ to aluminum oxide is an endothermic process with theoretical heat $\Sigma\Delta H_{298^\circ\text{K}} = 9.63 \text{ MJ/kg}_{\text{alumina}}$ which requires considerable amount of heat. As compared to conventional Al_2O_3 calcination from aluminum hydroxide ($\text{Al}(\text{OH})_3$), heat consumption and the specific volume of exhaust gases is about 4 times higher.

For experiments with aluminum chloride calcination, a laboratory unit (Fig. 1) was assembled, including a tubular kiln (1), six carborundum heaters (2), control block (3), and reaction chamber (4). The control block is equipped with temperature indicator (5) and control elements for zero setting (6), and setting of the required temperature (7).

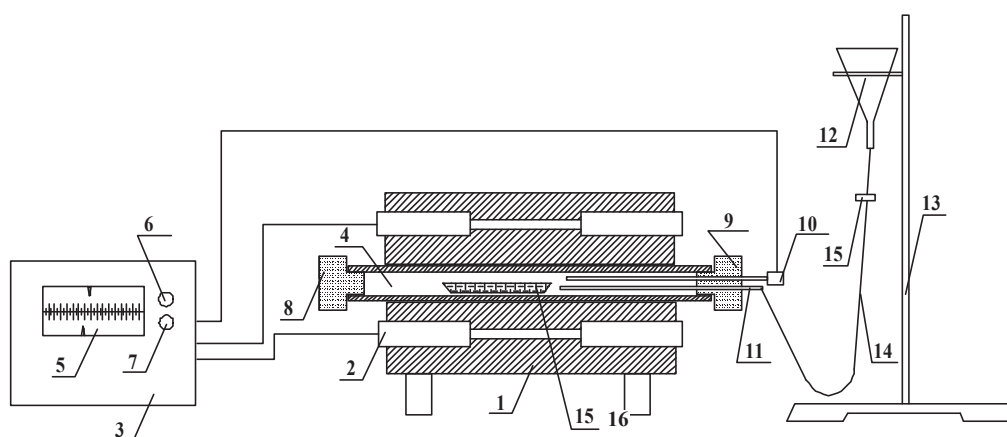


Figure 1. Laboratory tubular kiln for ACH calcination.

The reaction chamber is equipped with lids (8 and 9) made of lightweight fireclay. The lid (9) is equipped with thermocouple (10) and socket for steam or water supply (11). A water tank (12) is installed on a stand (13) and is connected by flexible hose (14) to a supply socket (11). The hose (14) is equipped with an adjustable clamp (15) to control liquid flow rate into the reaction zone. The calcination of product was conducted in a corundum boat (16) installed in reaction chamber (4).

While assessing the results, first of all, residual Cl content in the product was considered. This is because of the harmful influence of increased Cl content on dioxins formation during electrolysis process.

Experiments with variation of chlorine content in the samples calcined at temperatures 650, 850 and 1000 °C and residence time 60 min with and without steam supply is presented in Fig 2. In these series of experiments the sample was heated to the specified temperature in the kiln.

As presented in Fig. 2, with a temperature increase to above 650 °C, a sharp reduction in chlorine content in the samples occurs. This fact was also noticed by other researchers [1, 2]. Further, as temperature goes up, the dechlorination process slows down. At very long residence times, the Cl can be removed completely [3, 4]. This effect was also revealed in industrial ACH calcination [5].

This problem can be solved in two different ways:

- Adjustment of alumina properties to modern smelter requirements. There are some ways to solve this problem, patents are pending in the Patent Office of Russia;
- Development of a new generation of cells suited for unique properties of this alumina.

Each approach is of interest.

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